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ORIGINAL ARTICLE

Comparison of physico-chemical, advanced oxidation and biological techniques for the textile wastewater treatment

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Abstract Toxic organic dye removal from the textile wastewater is a serious concern. It is difficult to choose a single or a combination of treatment techniques between various available options; each with certain advantages and drawbacks. Six different techniques were applied on the same textile wastewater to evaluate the most effective in terms of treatment efficiency. The three most important textile wastewater quality parameters of chemical oxygen demand (COD), total suspended solids (TSS) and color were made the basis of the comparison of different treatment techniques. Other critical parameters such as treatment time, ease of operation and chemical cost employed were also considered. No single biological or physico-chemical treatment technique was found capable of removing up to 80% of the influent COD, TSS and color simultaneously from the textile wastewater. The conventional activated sludge (CAS) treatment followed by effluent polishing with the sand filtration (SF) and activated carbon adsorption columns was proved to be the most promising with COD, TSS and color removal efficiencies of 81.6%, 88.5% and 94.5% respectively. Moreover this combination of techniques enjoys lower chemical cost, medium operation time and fewer difficulties in the process control. Hence, the combination is recommended for the treatment of the textile effluents.

1. Introduction

The pollutants in the untreated wastewater need to be removed for the safe disposal into the fresh water bodies [1]. The uncontrolled industrial and urban wastewater discharge has posed a significant negative impact on the streams' and rivers' water quality [2]. The textile industry affects environment in two ways; by its huge water consumption and by the complexity

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of the chemicals used in the various manufacturing processes [3,4]. The textile wastewater may cause severe hazardous contamination of the water bodies [5]. Moreover, increasing population with the corresponding increasing water demand provokes the need of the treated wastewater reuse in the agriculture and industry [6].

One of the important textile processes is the color dying of the clothes with the organic dyes that increase the chemical oxygen demand (COD) of the water. These dyes constitute a serious aesthetic problem in the public opinion and restrict the downstream reuse of the wastewater [7], because of the low biodegradability of many chemicals and dyes employed in various textile processes; the biological treatment alone is not a very good option [8]. Also, the conventional biological treatment has certain disadvantages such as sludge production, high energy demand and frequent maintenance requirement [9]. However, the addition of various adsorbents and chemicals directly into the activated sludge systems, to form the hybrid systems, for improving the color removal efficiency is reported [10,11]. These systems can be a good option for the textile wastewater treatment, but, the contamination of activated carbon in the effluent, loss of the activated carbon with discharge sludge and the increase in sedimentation time are some of the serious concerns associated with the hybrid systems [12].

The physico-chemical treatment processes such as coagulation-flocculation, advanced oxidation and electrochemical techniques are effective, quick and compact but are not generally employed due to the associated high chemical and operational costs as well as complex sludge generation [13,14]. As compared with the aluminum salts; iron salts coagulate in a wider pH range and form heavier flocs with relatively less danger in the case of coagulant overdose [15]. The use of the Fenton's reagent for the treatment of textile wastewater is one of the most advanced oxidation processes [16]. The high removal efficiencies of Fenton is due to the formation of strong hydroxyl radical ($OH^\bullet$) and the oxidation of Fe^{2+} to Fe^{3+} with the formation of ferric hydro complexes; which simultaneously acts as a coagulant and oxidant [17]. The $OH^\bullet/H_2O$ has a very strong oxidation potential of $+2.73$ V but it leaves a yellowish color in the treated wastewater. Adsorption produces high quality product water by adsorbing the cationic, mordant and acid dyes from the textile wastewater. However, the activated carbon is expensive and has to be reactivated; otherwise the disposal of the concentrate needs to be considered as well. Moreover; the granular activated carbon (GAC) can only maintain its adsorption capacity for a short time after the available adsorption sites are exhausted with adsorbed pollutants [18].

The advantage of the sequencing batch reactor (SBR) is the single tank design and the flexibility allowing them to meet different treatment objectives. The SBR has five major steps of fill, react, settle, decant and idle. The SBRs can be designed and operated to attain the enhanced nitrogen, phosphorus and ammonia removal in addition to the removal of total suspended solids (TSS) and COD [19].

Individually, all the treatment processes are associated with certain advantages and disadvantages and a very sound knowledge of the chemistry and processes is required to choose the most suitable for the real time applications. Most of the literature available deals with the synthetic textile wastewater treatment that comprises of only one or few organic dyes and readily biodegradable organics dissolved in de-ionized (DI) water. The real textile wastewater chemistry and behavior is entirely different due to the combination of various dyes, chemicals, suspended particles, nutrients and bacteria in it. This study compares the effectiveness of six different treatment techniques employed on the real textile wastewater. Based on literature, the three most important textile wastewater quality parameters of COD, TSS and color were made the basis of the comparison. Moreover, important designing factors such as treatment time, operational control and chemical cost were also given equal consideration in the final recommendations. This uniqueness of this study is to conclude the best individual and combination of techniques based on real time experimental results.

2. Materials and methods

2.1. Sampling, chemicals and analytical methods

The wastewater for this study was sampled from the Paharang drain Faisalabad, Pakistan. More than 200 textile industries discharge their untreated effluent in this drain. The 24 h composite samples were collected and stored at 4 °C to retard any biological activity. All the analytical work was conducted according to the procedures prescribed in the standard methods [20]. The chemicals, activated carbon and test kits used in the study were purchased from Sigma Aldrich and HACH. All the chemicals were used as such without any change in their chemistry or purity. All chemical solutions were prepared in the DI water.

2.2. Conventional activated sludge (CAS) and sequencing batch reactor setup

The seed activated sludge for the CAS reactor and the SBR was collected from the I-9 sewage treatment plant, Islamabad, Pakistan. The sludge was acclimatized for 2 weeks with the textile wastewater and then was introduced in the CAS reactor. A poly acrylic, transparent vessel having a working volume of 30 L was used as the CAS reactor. The reactor was operated continuously for 7 weeks with hydraulic retention time (HRT) of 8 h and solid retention time (SRT) of 30 days. Continuous flow at 90 L/day was subjected to the reactor using a peristaltic pump (Model: SP-311, VELP) with a wattage of 20 W. The aeration was provided at the rate of 2 L/min, with aeration pump (Model: AK-808, China) and diffusers, to maintain the desired activated sludge mixing and maintaining the dissolved oxygen (DO) level of 2 mg/L in the reactor. DO was measured using a portable DO meter (Model: Sension 6, HACH). The temperature of the sludge was maintained at 23 ± 1 °C using an automatic heater (Model: PR 580, China) immersed inside the reactor. The reactor was operated at the wastewater normal pH of 8.5 ± 1. The SBR consisted of a transparent vessel with 1.5 L effective volume. The SBR was placed in a water bath at 23 ± 1 °C and the whole operation was performed at normal pH (8.5 ± 1) of the wastewater. The aeration was provided at a constant flow of 0.95 L/min at a pressure of 0.1 bars. Aeration helped in maintaining a DO level between 2.5 and 3.5 mg/L and providing sufficient mixing of the sludge to keep it in suspension. The SBR was operated for 3 weeks at 8 h HRT without any sludge wasting. The SBR was aerated for 6.75 h and then a combined settling plus decantation was employed for 0.75 h followed by 0.5 h filling.

2.3. Sand filtration (SF) and activated carbon adsorption columns

For 2 weeks, the treated effluent of the CAS reactor was passed through the SF and GAC adsorption columns for further polishing. The configuration of the two columns is shown in Fig. 1. The GAC used in the column was derived from coal, activated with steam and had an average diameter of approximately 1 mm, as mentioned by the supplier. Gravel was used for supporting the fine sand in the SF column. The finer sand of 100 mesh size was above 80 mesh sand. The configuration of both columns was adopted by trial and error method to elute continuously the CAS treated effluent. Columns were first flushed with DI water for 8 h to remove all the trapped impurities and fine particles and then were used in the study. The same columns were used for 2 weeks to assess the trend of their efficiency with the operation time.

2.4. Coagulation, oxidation and adsorption experiments

During all these batch experiments, 1 L of the textile wastewater was taken in each of the 6 jars of the jar test apparatus; 2 min coagulation at 120 rpm followed by 20 min flocculation at 20 rpm and half hour settling were applied. All jar test studies were carried out at a pH of 8.5 ± 1 and temperature of 23 ± 1 °C.

3. Results and discussion

3.1. Wastewater chemistry and potential treatment options

Table 1 summarizes the average wastewater characteristics of the Paharang drain over a year period elaborately discussed in our previous study [21].

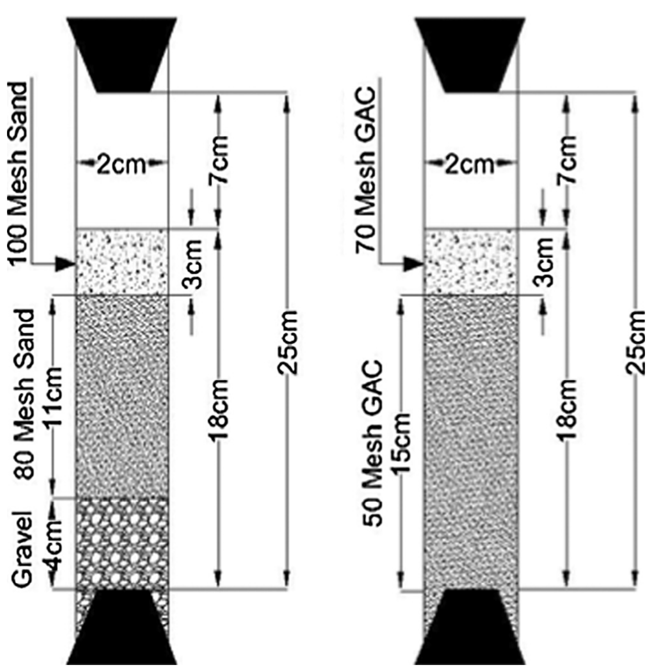

Figure 1 Configuration of the sand filtration and activated carbon adsorption columns.

Table 1 Average physico-chemical and biological characteristics of the sample wastewater.

Parameters	Units	Average[a] value ± SD
Temperature	Celsius	25.4 ± 7.6
BOD	mg/L	224.6 ± 40.7
COD	mg/L	433.7 ± 35
pH	–	8.5 ± 1
DO	mg/L	0.84 ± 0.31
TSS	mg/L	244 ± 76
VSS	mg/L	135 ± 17.3
Color	Pt-Co	456 ± 22.6
TN	mg/L	55.8 ± 23.7
TP	mg/L	13 ± 2.1
TDS	mg/L	2570 ± 490
Sulfates	mg/L	412 ± 26
Chloride	mg/L	846 ± 266
Oil and grease	mg/L	28 ± 3.4

[a] An average of 10 samples.

Looking at Table 1, chemistry of the wastewater and the potential treatment options may be revealed. The biological oxygen demand (BOD)/COD ratio of 0.51 suggests the partial treatability of this wastewater through biological methods, also, the COD:N:P of 100:13:3 depicts sufficient nutrients availability for the aerobic bacteria growth and sustenance. The volatile suspended solids (VSS)/TSS ratio of 0.55 demonstrates that 45% of the influent TSS cannot be removed by the biological treatment. Moreover; the high concentration of the oil and grease discourages the idea of only biological treatment, so, some pre- or post-physico-chemical treatment is essential. The high total nitrogen (TN) concentration of 55.8 ± 23.7 mg/L suggests strong possibility of the presence of azo dyes. Since the aerobic biological treatment cannot remove the azo bond so, some combine aerobic and anaerobic treatment may be a better option.

3.2. Activated sludge, sand filtration and adsorption effect on the pollutants removal

Fig. 2 shows the COD removal after three stages of the treatment. Improvement of the CAS efficiency from 45% to 57% in 7 weeks could be attributed to the continued bacterial acclimatization with the influent wastewater. The SF and GAC columns were able to remove only up to 9% and 19% of the influent COD, respectively. Jointly the maximum COD removal attained was 81.6% and the remaining 18.4% of the influent COD went untreated with the effluent. Fig. 3 demonstrates the TSS removal after three stages of the treatment. The CAS, SF and GAC jointly achieved a maximum of 88.5% TSS removal, while the remaining 12.5% TSS flushed out with the treated effluent. Fig. 4 describes the color removal efficiencies. A maximum of 94.5% color removal was achieved after all three stages of the treatment and 15.5% of the influent color stayed in the final effluent. The efficiencies of both the SF and GAC columns followed a declining trend. This may be attributed to the trapped organics on the inert sand and carbon surfaces, which make it slippery and allow the incoming contaminants to pass through the column with fewer chances of adsorption and entrapment.

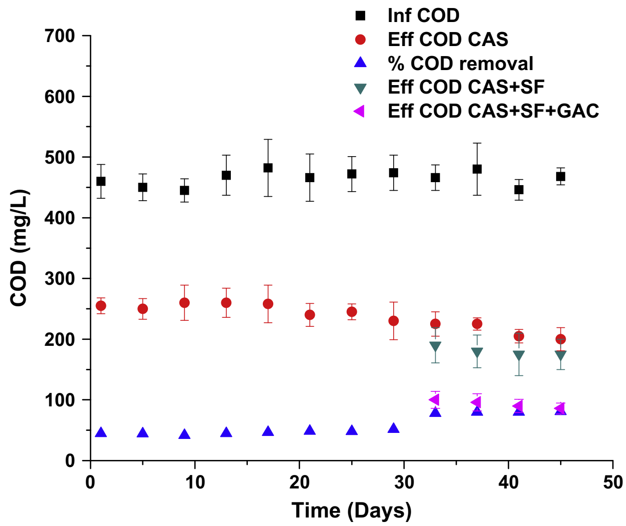

Figure 2 COD removal after biological treatment, sand filtration and GAC adsorption.

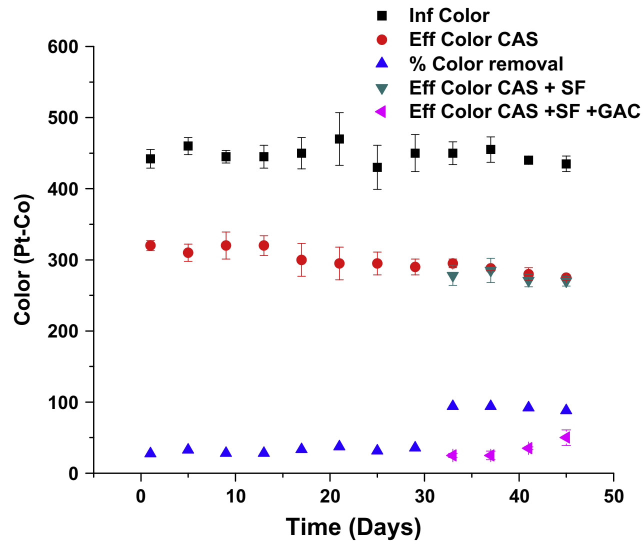

Figure 4 Color removal after biological treatment, sand filtration and GAC adsorption.

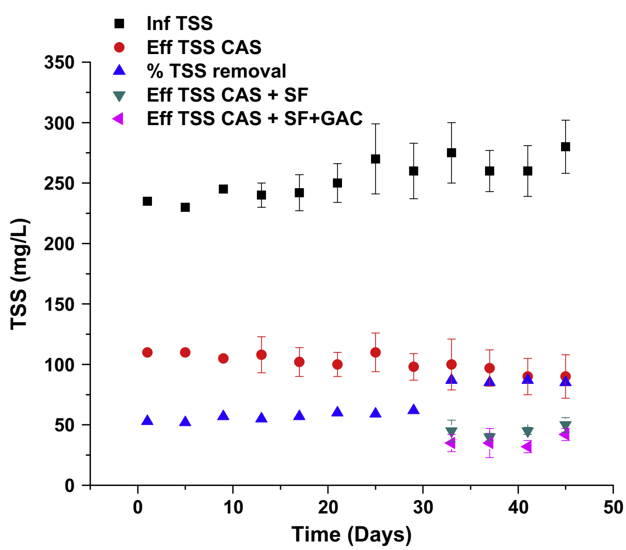

Figure 3 TSS removal after biological treatment, sand filtration and GAC adsorption.

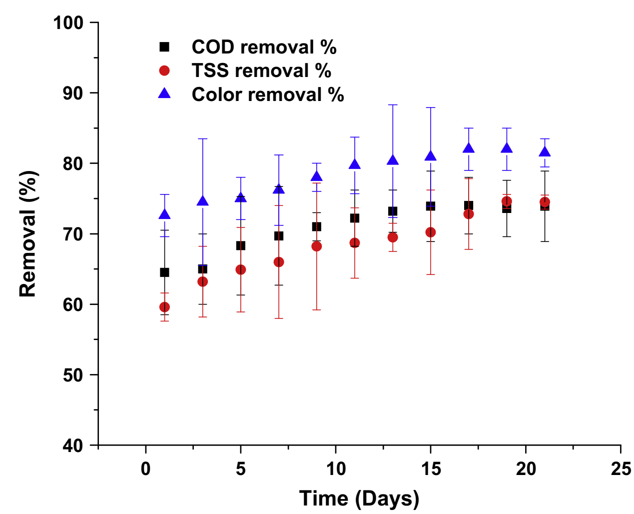

Figure 5 Effectiveness of SBR in contaminant removal.

3.3. Sequencing batch reactor effect on the pollutants removal

Fig. 5 demonstrates that the removal efficiencies improved with the operation period of the SBR to a maximum before becoming constant. The reason may be the rapid increase of the mixed liquor volatile suspended solids (MLVSS) concentration in the SBR from 2300 to 2900 mg/L, followed by a decelerated increase and final stabilization at 3200 mg/L. The maximum removal efficiencies lingered at 74%, 74% and 81% for the COD, TSS and color; respectively. High efficiency of the SBR compared to CAS is mainly due to the augmentation of slowly growing anoxic bacteria which are specialized in nitrogen and phosphorous removal. In azo-dyes; the azo bond (—N═N—) is responsible for the resistance against aerobic bacterial attack. Under anoxic conditions the cleavage of azo bond causes a reduction in the size of dye molecule which encourages dye hydrolysis followed by biodegradation.

3.4. Coagulation, oxidation and batch adsorption effect on the pollutants removal

Table 2 summarizes the results of coagulation, oxidation and adsorption batch experiments. The initial COD, TSS and color values in batch experiments were 460 mg/L, 250 mg/L and 440 Pt-Co respectively. The 20% and 16.4% TSS removal at zero alum and GAC dose depicts the potential of sedimentation as pre-treatment technique for treating a fragment of this wastewater. Above 20 mg/L dose further addition of alum caused an increase in the effluent COD. This increase was probably due to the presence of un-used aluminum hydroxide complexes, formed by alum dissolution into the water, which affect the turbidity, pH and consequently the COD of the solution. Increasing alum dose above 20 mg/L did not increase the color removal efficiency much. This confirms the interdependence of color and COD in the wastewater. The increase of 13% TSS

Table 2 Effectiveness of the coagulation, oxidation and adsorption treatment techniques.

Alum dose (mg/L)	COD removal (%)	TSS removal (%)	Color removal (%)	GAC Dose (g/L)	COD removal (%)	TSS removal (%)	Color removal (%)
0	3.9	20	4.6	0	2.2	16.4	1.1
10	56.5	52	29.5	2	37.4	24.4	34.5
20	58.7	60.4	34.1	4	54.3	31.2	60.0
30	34.8	73.2	34.5	6	56.3	32	68.6
40	39.1	59.6	31.6	8	49.1	30.8	78.6
50	43.5	61.2	33.0	10	50.4	32.8	88.2

H_2O_2 dose (ml/L)	$FeSO_4$ dose (mg/L)	COD removal (%)	TSS removal (%)	Color removal (%)
0	10	21.7	24.8	19.3
0.176	10	34.1	36.4	24.3
0.352	10	57.2	61.2	18.2
0.440	10	67.8	75.2	11.4
0.440	0	14.1	16	20.2
0.440	6	39.8	46.4	18.2
0.440	10	70.0	72.4	13.2

Table 3 Summary of efficiencies of the six techniques for textile wastewater treatment.

Criteria	CAS	CAS + SF +GAC	SBR	Alum coagulation	Fenton's oxidation	GAC adsorption
Maximum COD removal efficiency (%)	57	81.6	74	58	68	56
Maximum TSS removal efficiency (%)	68	88.5	74.6	73	72	32
Maximum Color removal efficiency (%)	37	94.5	81.5	34	24	88
Time for maximum removal (h)	8	8	8	2	2	2
Chemical cost for 1 m^3 wastewater treatment (US $)	0	0.25	0	1.30	2.50	1.50
Operational difficulty and process control (low–medium–high)	Low	Low	Med	Med	High	Med
Total points earned/100	62	75	67.5	59.2	45.6	59.7

removal efficiency from 20 to 30 mg/L alum dose is significant, but it is related to the corresponding 50% increase in coagulant amount and 24% loss in the COD removal efficiency. So, 20 mg/L alum dose may be regarded as the optimum.

The activated carbon in batch mode depicted maximum of 88% color removal. It is interesting to note that the efficiency for available color removal varied by only 3% between the column mode (91%) and the batch mode (88%) adsorption. So, the mixing or static forms do not make much difference in GAC behavior and it depends more on available active adsorption sites. The same theory can be proved by comparing 50% and 56% COD removal and 28% and 32% TSS removal in the column and the batch modes respectively. This also confirms that the adsorption cannot remove the contaminants individually and has to be accompanied by certain pre- or post-treatment techniques. The color removal in the batch mode increased proportionally with the increasing GAC dose but the dose was not increased beyond 10 g to formulate significant comparison with the column mode; which also used 10 g of the GAC. Also, the increasing GAC dose was ineffective on COD and TSS removal.

It was found that the 0.440 ml/L dose of H_2O_2 produced highest removal with the constant $FeSO_4$ dose of 10 mg/L. In next step, keeping H_2O_2 dose constant the $FeSO_4$ dose was optimized in the lower range (limited results shown). Again, the highest $FeSO_4$ dose of 10 mg/L was proven best. It is interesting that with the increasing concentration of Fenton the color removal decreased either due to the yellowish color of Fenton itself or due to the increase in TSS removal which depletes the excess solids inside the system that serve as a biosorbent for color dyes [22].

Due to the high chemical cost of both reagents and ineffectiveness over color removal, it was not practically feasible to go above this concentration. Looking carefully at Table 3, it is revealed that individually $FeSO_4$ was more effective compared to H_2O_2 in terms of contaminant removal. It is interesting to note that Fenton's reagent performs better at lower pH values of 3–4 [23], but in this study for the sake of comparison with the other techniques the pH was kept at 8.5 ± 1.

Table 3 summarizes the maximum efficiencies of all six treatment techniques along with operational time, chemical cost and operational control as the criteria parameters. The chemical costs were calculated based on the actual costs of the chemicals employed during the experiments. The operational difficulty and process control was divided into three categories of low, medium and high. It was calculated based on operator's exposure time to the system, harmfulness of the chemicals used, handling and quality of the sludge produced and the ease of operation. The relative difficulties and process control are suggested as per authors own understanding through literature review and experiments under this study. Point based calculation was done for all six techniques with each of the six criteria being allotted equal points of 16.6. For COD, TSS and color removal the efficiency was multiplied with 16.6 to calculate the points. For the other three parameters relative calculations were done using multiplication factors and finally subtracting the final answer from 16.66. The total points earned by each technique out of 100 are reported in the final row of Table 3.

4. Conclusions

No single biological or physico-chemical treatment technique was found capable of removing up to 80% of the influent COD, TSS and color simultaneously from the textile wastewater. However, the combination of conventional activated sludge treatment followed by sand filtration and activated carbon adsorption demonstrated highest organics (81.6%) and color (94.5%) removal with low operational difficulty and nominal chemical cost. So, this combination of techniques is recommended for the textile wastewater treatment. As an individual technique sequencing batch reactor proved itself promising in contaminant removal with zero chemical cost and medium operational control. So, if less operational chemical cost is available then the SBR may be a preferred treatment option. The 20% TSS removal by just mixing the wastewater and allowing it to settle derives the attention toward the potential of primary sedimentation as a pre-treatment technique.

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References

[1] R. Devi, R.P. Dahiya, COD and BOD removal from domestic wastewater generated in decentralised sectors, Bioresour. Technol. 99 (2008) 344–349.
[2] M. Qadir, N.R. Malik, Z.S. Husain, Spatio-temporal variations in water quality of Nullah Aik-tributary of the river Chenab, Pakistan, Environ. Monit. Assess. 140 (2007) 43–59.
[3] I. Arslan-Alaton, I. Alaton, Degradation of xenobiotics originating from the textile preparation, dyeing and finishing industry using ozonation and advanced oxidation, Ecotoxicol. Environ. Saf. 68 (2007) 98–107.
[4] G.R.N. Bidhendi, A. Torabian, H. Ehsani, N. Razmkhah, Evaluation of industrial dyeing wastewater treatment with coagulants and polyelectrolyte as a coagulant aid, Iran J. Environ. Health Sci. Eng. 4 (2007) 29–36.
[5] Y.M. Slokar, M.A. Marechal, Methods of decoloration of textile wastewaters, Dyes Pigm. 37 (1998) 335–356.
[6] M.S. Nawaz, G. Gadelha, S.J. Khan, N.P. Hankins, Microbial toxicity effects of reverse transported draw solute in the forward osmosis membrane bioreactor (FO-MBR), J. Membr. Sci. 429 (2013) 323–329.
[7] N.D. Lourenco, J.M. Novais, H.M. Pinheiro, Effect of some operational parameters on textile dye biodegradation in a sequential batch reactor, J. Biotechnol. 89 (2001) 163–174.
[8] J.G. Montano, N. Ruiz, I. Munoz, X. Domenech, J.A. Garcia-Hortal, F. Torades, J. Peral, Environmental assessment of different photo-Fenton approaches for commercial reactive dye removal, J. Hazard. Mater. 138 (2006) 218–225.
[9] S.K. Liehr, A.R. Rubin, B. Tonning, Natural treatment and onsite processes, Water Environ. Res. 76 (2004) 1191–1237.
[10] A. Pala, E. Tokat, Color removal from cotton textile industry wastewater in an activated sludge system with various additives, Water Res. 36 (2002) 2920–2925.
[11] S. Sirianuntapiboon, J. Sansak, Treatability studies with granular activated carbon (GAC) and sequencing batch reactor (SBR) system for textile wastewater containing direct dyes, J. Hazard. Mater. 159 (2008) 404–411.
[12] B.P. Flynn, J.G. Stadnik, Start up of a powdered activated carbon activated sludge treatment system, J. Water Pollut. Con. Feder. 51 (1979) 358–369.
[13] S.M. Ghoreishi, R. Haghighi, Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent, J. Chem. Eng. 95 (2003) 163–169.
[14] S. Sirianuntapiboon, K. Chairattanawan, S. Jungphungsukpanich, Some properties of a sequencing batch reactor system for removal of vat dyes, Bioresour. Technol. 97 (2006) 1243–1252.
[15] F.S. Rênnio, F.M. Regina, J.J. Humberto, Comparison of coagulants and coagulation aids for treatment of meat processing wastewater by column flotation, Bioresour. Technol. 99 (2008) 8221–8225.
[16] S. Kang, C. Liao, S. Po, Decolourization of textile wastewater by photo-Fenton oxidation technology, Chemosphere 41 (2000) 1287–1294.
[17] J.J. Lin, X.S. Zhao, D. Liu, Z.G. Yu, Y. Zhang, H. Xu, The decoloration and mineralization of azo-dye C.I. Acid Red14 by sonochemical process: rate improvement via Fenton's reactions, J. Hazard. Mater. 157 (2008) 541–546.
[18] O. Aktas, F. Cecen, Bioregeneration of activated carbon: a review, Int. Biodeterior. Biodegrad. 59 (2007) 257–272.
[19] D.S. Lee, G. Sin, G. Insel, I. Nopens, P.A. Vanrolleghem, Model based optimization of a sequencing batch reactor for advance biological wastewater treatment, Stud. Surf. Sci. Catal. 159 (2006) 165–168.
[20] Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association (APHA), Washington, 2005.
[21] M.S. Nawaz, S.J. Khan, Effect of HRT on SBR performance for treatability of combined domestic and textile wastewaters, J. Chem. Soc. Pak. 35 (2013) 527–532.
[22] S. Sirianuntapiboon, Application of granular activated carbon-sequencing batch reactor (GAC-SBR) system for treating pulp and paper industry wastewater, Thammasat Int. J. Sci. Technol. 7 (2002) 20–29.
[23] C.T. Benati, C.R.G. Tavares, T.A. Guedes, Optimization of Fenton's oxidation of chemical laboratory wastewaters using the response surface methodology, J. Environ. Manage. 80 (2006) 66–74.